Sorption Kinetics and Equilibria of Organic Pesticides in Carbonatic Soils from South Florida

P. Nkedi-Kizza,* D. Shinde, M. R. Savabi, Y. Ouyang, and L. Nieves

ABSTRACT

A batch reactor was used to determine sorption kinetic parameters (k_2, F, and K^*) and the equilibrium sorption coefficient (K). The two-site nonequilibrium (TSNE) batch sorption kinetics model was used to calculate the kinetic parameters. Two probe organic pesticides, atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine] and diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] were studied using three carbonatic soils from South Florida (Chekika, Perrine, and Krome), one noncarbonatic soil from Iowa (Webster), and one organic soil (Lauderhill) from South Florida. Carbonatic soils contained more than 600 g kg^{-1} CaCO$_3$. Sorption is initially very fast up to 3 h and then slowly reaches equilibrium. All soil–chemical combinations reached sorption equilibrium after about 24 h and all sorption isotherms were linear. The sorption kinetics data were well described by the TSNE model for all soil-chemical combinations except for the marl soil data (Perrine–Atrazine), which were better described by the one-site nonequilibrium (OSNE) model. Diuron, with higher K, undergoes slower sorption kinetics than atrazine. The Lauderhill soil containing organic carbon (OC) of 450 g kg^{-1} exhibited slowest sorption kinetics for both pesticides. An inverse relationship between k_2 and K was observed for atrazine and diuron separately in Chekika, Webster, and Lauderhill soils but not in Perrine and Krome soils. The sorption kinetic parameters were used to distinguish the sorption behavior between atrazine and diuron and to identify differences between soils. Normalizing the sorption coefficient (K) to OC showed that atrazine and diuron had K_{oc} values in carbonatic soils that were a third of reported literature values for noncarbonatic soils. Using existing literature K_{oc} values in solute transport models will most likely underestimate the mobility of atrazine, diuron, and other neutral organic chemicals in carbonatic soils.

S URFACE AND GROUND WATER contamination resulting from application of agricultural chemicals to soils is a national environmental concern. Assessment of pesticide sorption during transport is a prerequisite for minimizing their potential mobility in the vadose zone (Selim, 2004). In South Florida, approximately 13 230 Mg of pesticides are used each year, mainly in agriculture (Miles and Pfeuffer, 1997). In a nationwide survey of pesticide loading to coastal regions, Miami-Dade County in South Florida ranked second in agricultural application (Pait et al., 1992). The Miami-Dade County agricultural area is of particular importance due to its proximity to the Everglades National Park (Downing et al., 2004). Of particular concern is the shallow soil depth (15–60 cm)

of major agricultural soils that provides only a thin protective layer of soil to the underlying high water table. Very little data are available in the literature for the sorption kinetics and equilibria parameters of pesticides in carbonatic soils. Sorption kinetics and equilibria parameters play an important role in determining the fate and transport of pesticides in the environment. Application practices for pesticides, combined with the high annual rainfall in South Florida, could result in significant amounts of pesticides reaching nontarget sites.

Atrazine is one of the most widely detected herbicides in surface and ground water in the United States. It is usually applied to the soil surface and its fate in soil depends on the interaction between its molecules and soil components (Ben-Hur et al., 2003). Diuron is among the top 10 pesticides frequently detected in shallow ground water and is characterized as a potential threat to ground water resources due to its moderate water solubility, low tendency to sorb to soils, and relatively long half-life (Field et al., 2003). The drinking water maximum concentration level (MCL) for atrazine is 3 µg L^{-1} (USEPA, 1998). Although no MCL is established for diuron in the United States, the health advisory limit is 10 µg L^{-1} (USEPA, 1987).

Two of the major factors known to influence sorption of pesticides are soil properties and the molecular characteristics. Sorption of neutral organic pesticides, such as atrazine and diuron, depends primarily on soil organic carbon (OC) content (Madhun et al., 1986). Sorption determines whether the pesticide will persist, be transported, and pollute the underlying ground water (Rao and Hornsby, 1983). Strongly adsorbed and persistent pesticides that have large (K_{oc}) values are likely to remain near the soil surface. In contrast, weakly adsorbed but persistent pesticides (small K_{oc}) may be readily leached through the soil and are more likely to contaminate ground water. Atrazine and diuron are moderately persistent with half-life of 60 d for atrazine and 90 d for diuron and K_{oc} values are 100 for atrazine and 400 for diuron (Nkedi-Kizza et al., 1985; Wauchope et al., 1992).

Experimental investigations of sorption processes are often conducted in batch systems rather than dynamic systems, to distinguish the sorption process from hydrodynamic dispersive effects (Pedit and Miller, 1994). Batch experiments are also used to obtain data for rates of intermediate and slow sorption (Wu and Gschwend, 1986). Batch experiments utilize static conditions in which forward and reverse reactions are allowed to proceed until an equilibrium condition is established (Harter, 1991). Modeling efforts focusing on describing the retention mechanisms of pesticides in the soil environment

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Abbreviations: OC, organic carbon; OSNE, one-site nonequilibrium; TSNE, two-site nonequilibrium.

have generally been based on results from batch sorption experiments. Batch data based on 24-h adsorption are commonly regarded as a measure of equilibrium-type retention. Kinetic data, which are measured infrequently, have the advantage of taking into account possible time-dependent reactions for adsorption, release, or desorption. Nonequilibrium conditions may be caused by the heterogeneity of sorption sites and slow diffusion to sites within the soil matrix, or organic matter (Brusseau et al., 1991; Selim, 2004).

A variety of chemical and physical nonequilibrium processes affect sorption and transport of pesticides in the subsurface (Nielsen et al., 1986; Aharoni and Sparks, 1991). Chemical nonequilibrium models consider adsorption on some of the adsorption sites to be instantaneous, while adsorption on the remaining sites is governed by first-order kinetics (Selim et al., 1976; Cameron and Klute, 1977; Van Genuchten, 1981; Nkedi-Kizza et al., 1984; Ma and Selim, 1997).

The main objective of this study was to determine sorption kinetics from batch experiments for neutral organic chemicals (i.e., atrazine and diuron) and to ascertain sorption characteristics in carbonatic and non-carbonatic soils. Such information is necessary for understanding soil pesticide mobility through runoff and leaching and for preventing potential contamination of water resources.

MATERIALS AND METHODS

Soils

Carbonatic Soils

The Chekika gravelly loam (loamy-skeletal, carbonatic, hyperthermic Lithic Udorthents) series consists of very shallow, somewhat poorly drained, moderately permeable soils over limestone. Soils formed by scarification of outcrops of oolitic limestone, and the marly sediments that partially cover the limestone and fill the many cavities or solution holes (USDA, 1996). These soils are adjacent to the Miami Ridge. Slopes are 0 to 2%. Chekika soils are transitional between well drained soils of the Miami Ridge and the poorly drained marl soils of Sawgrass Marsh in the Everglades. The water table is between 30 and 90 cm and is always within the limestone bedrock. The soils are cultivated to tomatoes, beans, corn, malanga, and limes as the principal crops. Geographically associated soils include Krome and Perrine.

The Krome (loamy-skeletal, carbonatic, hyperthermic Lithic Udorthents) series consists of very shallow, moderately well drained, moderately permeable soils over limestone. Soils formed by scarification of outcrops of oolitic limestone, and the loamy residuum that partially covers the limestone and fills the many cavities or solution holes (USDA, 1996). These soils

are on broad areas of the Miami Ridge. Slopes are predominantly 0 to 2% but range to 5%. The water table is between 1 and 1.5 m and is also always within the limestone bedrock. The soils are cultivated and tomatoes, beans, avocadoes, and limes are the main crops.

The Perrine marl (coarse-silty, carbonatic, hyperthermic Typic Fluvaquents) series consists of moderately deep, poorly drained, moderately slowly to moderately permeable soils in lowlands along the Atlantic Coast of Peninsular Florida. The soils formed in calcareous silty and loamy sediments of marine or freshwater origin over limestone (USDA, 1996). Slopes are less than 1%. The areas that have been drained, or have controlled water regimes, are used for growing vegetable crops, ornamental shrubs, and trees. Perrine soils are closely associated with Chekika, Krome, and Lauderhill.

Noncarbonatic Soils

The Webster (fine-loamy, mixed, superactive, mesic Typic Endoaquolls) series consists of very deep, poorly drained, moderately permeable soils formed in glacial till or local alluvium derived from till on uplands (USDA, 1996; Konen et al., 2003; Reuter and Bellb, 2003). Slope ranges from 0 to 3%. These soils are largely cultivated and cropped intensively with corn and soybeans. Small grain and hay are other major crops (Iowa State University Cooperative Extension Service, 1998). The soil was sampled from Iowa.

The Lauderhill (euic, hyperthermic Lithic Haplosaprists) series consists of very poorly drained soils that are 0.30 to 0.90 m thick over limestone. Lauderhill soils formed in organic deposits of freshwater marshes (USDA, 1996). Lauderhill soils are in freshwater marshes within peninsular Florida. Lauderhill soils are used for growing sugarcane, corn, sod, and improved pasture.

The five soils were selected for this investigation based on contrasting OC and CaCO₃ contents. Organic carbon content was determined by the method of Walkley and Black (1934). The thermogravimetric (TG) method (Nestler et al., 2003) was used to determine $CaCO_3$. Particle size distribution was measured by the pipette method (USDA, 1992). Sterile soils for sorption experiments were prepared by autoclaving once for 1 h at 120°C. Important physical and chemical properties of the soils that can influence atrazine and diuron sorption are listed in Table 1.

Pesticides

Atrazine and diuron were selected as probe pesticides because they are widely used in South Florida on carbonatic soils. We also have a large database on the two herbicides from our previous studies on sorption and transport in noncarbonatic soils. The selected properties of the two herbicides (Table 2) show a close resemblance in their molecular weight, total surface area, and hydrocarbonaceous surface area. As such we expected the herbicides to behave similarly during sorption in soils.

Table 1. Selected properties of soils used in this study.

Soil series	From	Sampling depth	Sand	Silt	Clay	Organic C	CaCO₃	pH†
		m			g kg⁻¹			
Chekika	Florida	0–0.20	610	250	140	45.30	660	7.4
Krome	Florida	0–0.20	590	310	100	25.60	630	7.4
Perrine	Florida	0–0.20	50	630	320	24.10	880	7.9
Lauderhill	Florida	0–0.30		muck		447.00	ND‡	7.0
Webster	Iowa	0–30	21.9	44.9	33.2	46.20	ND	7.3

† Measured in a 1:1 soil paste in 0.01 M CaCl₂.
‡ Not determined.

Table 2. Selected properties of atrazine and diuron.

Property	Atrazine	Diuron
Molecular weight, g	215.68	233.10
Total molecular surface area†, Å^2	219	219
Hydrocarbonaceous surface area†, Å^2	144	147
Aqueous solubility‡, µg mL^{-1}	33	42
Half-life‡, d	60	90

† Nkedi-Kizza et al. (1985).
‡ Wauchope et al. (1992).

Two-Site Nonequilibrium Batch Sorption Kinetics Model

The two-site nonequilibrium (TSNE) batch sorption kinetics model (see Appendix) was employed in this study to characterize sorption kinetics of atrazine and diuron in the five soils. Among the nonequilibrium processes influencing sorption is the possible division of sorption sites into two types. The two-site sorption concept presumes that sorption or exchange sites in soils can be classified into two fractions: Type 1, where sorption is assumed to be instantaneous, and Type 2, where sorption is considered time-dependent. In Fig. 9, the solid line represents reversible reaction (equilibrium sites) and the adsorbed fraction controlled by first-order sorption kinetics. The parameters and the governing equations for the TSNE model used to calculate batch sorption kinetics parameters (k_2, F, and K^*) are presented in detail in the Appendix.

Two equations were used to calculate the relative solution concentration (C/C_{in}) and the apparent sorption coefficient (K^*) as a function of time:

$$\frac{C}{C_{in}} = \frac{1}{R} + \left(\frac{1}{\beta R} - \frac{1}{R}\right) \exp[-(k_2/\beta)t] \qquad [1]$$

The three parameters (k_2, F, and K) are determined from the data using nonlinear curve fitting procedures on the C/C_{in} vs. time data (Eq. [1]). Thus a series of experiments with different C_{in} are normalized to one line by plotting C/C_{in} vs. time:

$$K^* = \frac{V}{M}\left\{\left[\frac{1}{R} - \left(\frac{1}{R} - \frac{1}{\beta R}\right) \exp\left(\frac{-k_2 t}{\beta}\right)\right]^{-1} - 1\right\} \qquad [2]$$

The apparent sorption coefficient (K^*) was calculated as a function of time using parameters C/C_{in} (from Eq. [1]), and V

and M that were measured before the sorption kinetics experiment was initiated.

Procedures for Sorption Experiments

Sorption isotherms were measured with the batch equilibration method (Nkedi-Kizza et al., 1985) at different times between 0.5 to 50 h. A solution of 10 mL of atrazine or diuron of initial concentration of 4, 8, 14, and 18 mg L^{-1} in 0.01 M CaCl$_2$, as a supporting electrolyte, was added to 10 g of autoclaved soils (in triplicates) in Teflon-lined centrifuge tubes. For the Lauderhill soil 0.5 g of soil were used. The tubes were shaken on a reciprocating shaker for different times at ambient temperature (22 ± 1°C). The tubes were then centrifuged at 6720 × g for 15 min and atrazine and diuron in clear supernatant solutions were analyzed by reverse phase high performance liquid chromatography (HPLC) with UV detection, using a Dionex (Sunnyvale, CA) 500 IC/HPLC system and Dionex-Peaknet 5.1 computing integrator. Atrazine and diuron were analyzed at 220 nm with absorbency set at 0.1 AU for all samples. The flow rate was 1 mL per minute. A C-18 column was used with a mobile phase of methanol, acetonitrile, and water (25:40:35). The amount of solute retained in the soil solution normalized to the initial solution concentration (C/C_{in}) was plotted versus time and the kinetic parameters were calculated using the TSNE model. The sorption coefficient (K) for each chemical–soil combination was calculated from an isotherm obtained by plotting S vs. C for each of the four initial solution concentrations measured at or after 24 h. All isotherms were described by the linear Freundlich isotherm ($S = KC$). The obtained K values were used as initial estimates in the TSNE model.

RESULTS AND DISCUSSION

Equilibrium Sorption Coefficient (K)

The data in Table 1 show that the soils of Miami-Dade County (Krome, Chekika, and Perrine) are highly carbonatic with over 600 g kg^{-1} CaCO$_3$ content. Perrine has the highest CaCO$_3$ content (880 g kg^{-1}) among the three soils. Considering that both atrazine and diuron are neutral at the pH of the experiments, any observed differences in sorption behavior can be attributed to differences in OC and CaCO$_3$ content in these soils. All
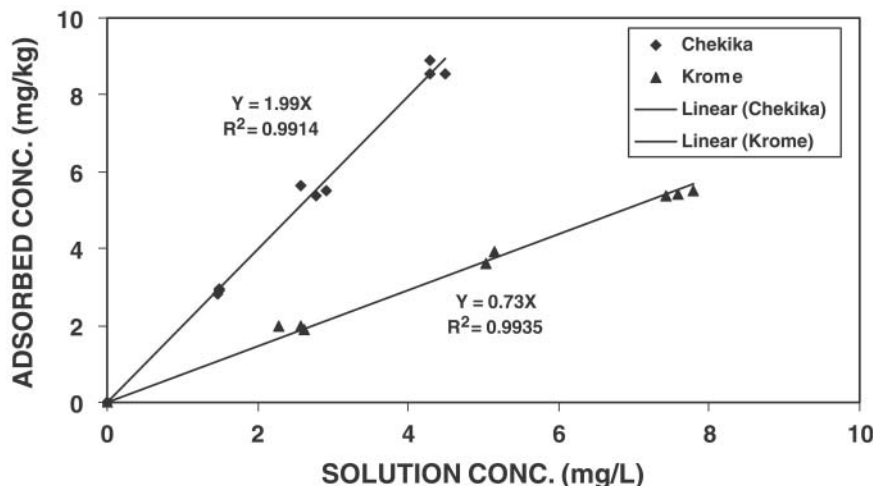

Fig. 1. Linear sorption isotherms for atrazine in Chekika and Krome soils.

Table 3. Soil-chemical parameters for atrazine and diuron, with standard error in parentheses.

Soil series	k_2	F	K From model	From isotherm	K_{oc}
	h^{-1}			L kg^{-1}	
			Atrazine		
Chekika	1.79 (0.52)	0.46 (0.30)	1.95 (0.09)	1.99 (0.09)	43
Krome	0.44 (0.18)	0.67 (0.05)	0.77 (0.03)	0.73 (0.05)	30
Perrine	2.57 (1.89)	0 (1)	0.49 (0.02)	0.63 (0.07)	23
Lauderhill	0.26 (0.03)	0.58 (0.03)	44.70 (0.90)	45.20 (1.13)	101
Webster	1.35 (0.08)	0.70 (0.04)	4.45 (0.07)	4.06 (0.07)	92
Literature					100†
			Diuron		
Chekika	0.18 (0.03)	0.53 (0.03)	6.10 (0.02)	6.36 (0.56)	138
Krome	0.12 (0.02)	0.31 (0.02)	3.25 (0.16)	3.25 (0.36)	127
Perrine	0.07 (0.03)	0.59 (0.04)	2.97 (0.24)	2.86 (0.26)	121
Lauderhill	0.09 (0.02)	0.18 (0.01)	189.03 (10.70)	190.03 (7.39)	424
Webster	0.15 (0.03)	0.49 (0.03)	16.61 (0.42)	17.21 (0.45)	366
Literature					400†

† Nkedi-Kizza et al. (1985), Wauchope et al. (1992).

sorption equilibrium isotherms were linear and equilibrium was attained in about 24 h. An example of the isotherms is presented in Fig. 1. The sorption coefficient (K) values calculated from the isotherms and those calculated using the TSNE model are presented in Table 3. For the two noncarbonatic soils, Webster and Lauderhill,

the K_{oc} values calculated by normalizing the equilibrium K with soil OC content were close to literature reported values for atrazine ($K_{oc} = 100$) and for diuron ($K_{oc} = 400$). However, in carbonatic soils atrazine and diuron had K_{oc} values of about one-third of literature K_{oc} values for noncarbonatic soils. For example comparing Chekika
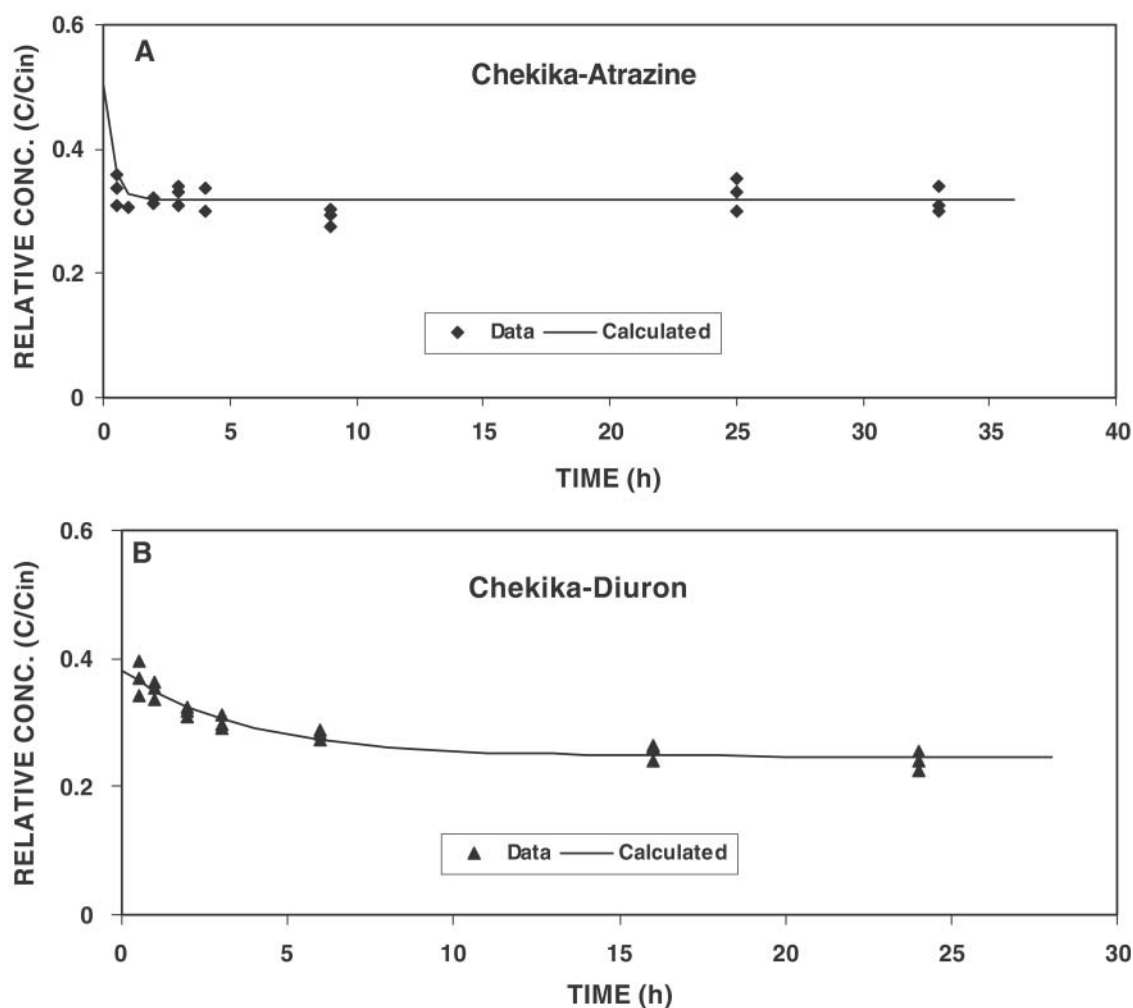

Fig. 2. Atrazine (A) and diuron (B) sorption kinetics in Chekika soil.
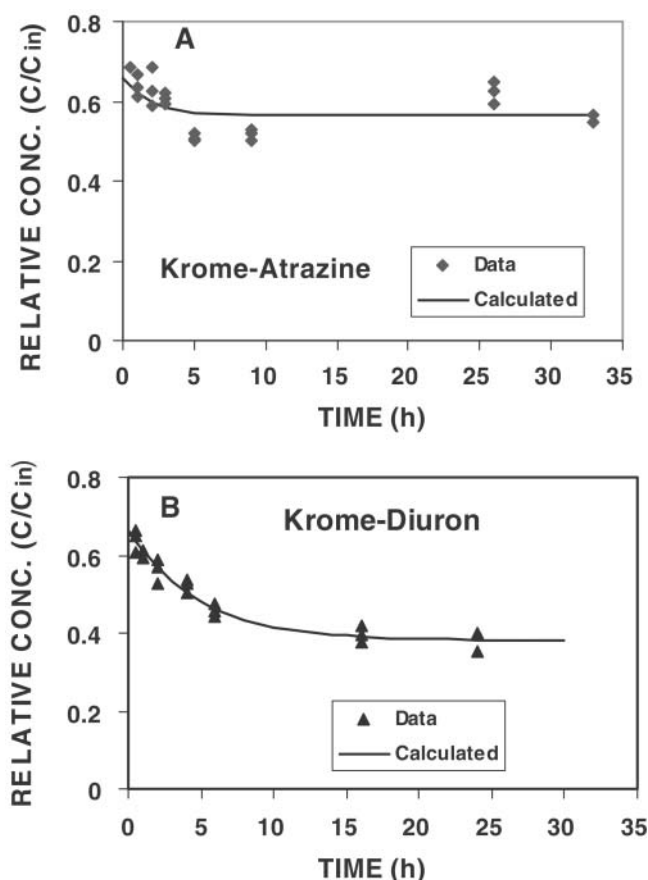
Fig. 3. Atrazine (A) and diuron (B) sorption kinetics in Krome soil.

soil (carbonatic) and Webster soil (noncarbonatic) that have similar OC contents, we observe that sorption coefficients were more than twice in Webster over Chekika for both atrazine and diuron (Table 3). This seems to suggest that the nature and makeup of OC somehow affects the sorption efficiency of OC in carbonatic soils. Although Perrine soil has nearly three times the clay content (Table 1) of the Krome and Chekika soils, clay content did not seem to have an effect on the sorption coefficient of atrazine and diuron at pH 7.
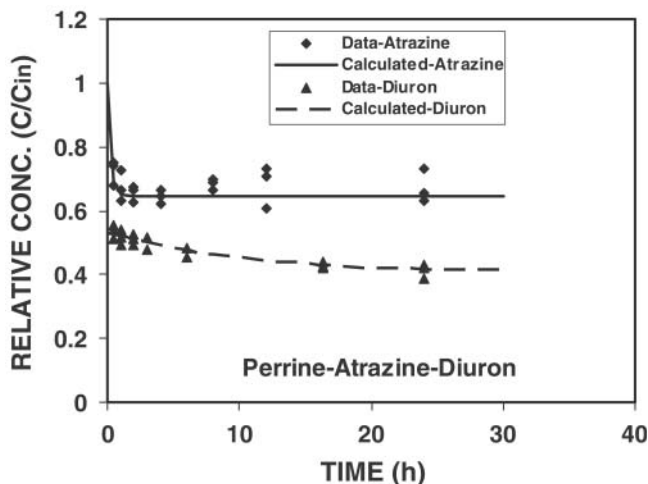

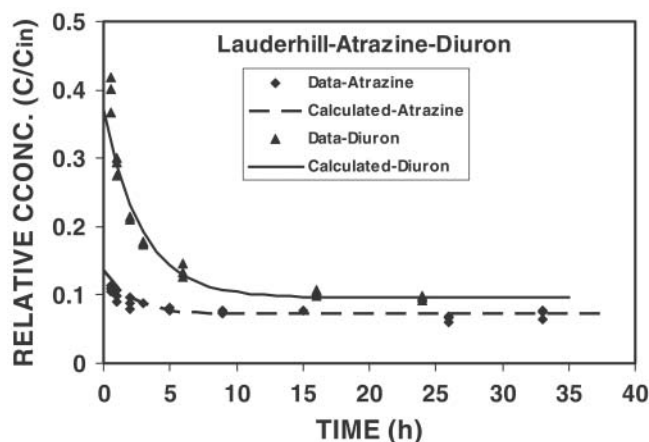Fig. 4. Atrazine and diuron sorption kinetics in Perrine soil.

Fig. 5. Atrazine and diuron sorption kinetics in Lauderhill soil.

Sorption Kinetics Parameters

Time-dependent sorption of atrazine and diuron by different soils with initial concentration of 8 mg L^{-1} are shown in Fig. 2 to 5. To avoid crowding of the figures with many data points we use the initial concentration of 8 mg L^{-1} to discuss the data because data analysis in Table 4 indicated that initial solution concentration did not affect the magnitude of the parameters (k_2, F, and K) calculated using Eq. [1]. However, the kinetic parameters presented in Table 3 were obtained from all four initial solution concentrations for each soil–chemical combination.

Data in Fig. 2 to 5 show that diuron sorption is more time-dependent in all soils than atrazine. Atrazine in most soils approaches equilibrium in less than 10 h, but diuron approaches equilibrium in about 15 h. This trend is further supported by the smaller k_2 values for diuron compared to atrazine (Table 3). The TSNE model described all sorption kinetics data well except for atrazine in Perrine soil. The sorption data for atrazine in Perrine soil show that the TSNE model is not valid since $F = 0$ (Table 3 and Fig. 4). The atrazine data in Fig. 4, in fact, can be described by the one-site nonequilibrium (OSNE) model. The OSNE model is a special case of the TSNE model, where all sorption sites are assumed to be time-dependent (Selim et al., 1976; Van Genuchten, 1981). Nzengung et al. (1997) used the OSNE model to describe sorption kinetics of several organic chemicals by organo-clays. The TSNE model, however, described the data well for diuron sorption in Perrine soil (Fig. 4 and Table 3). Note that Perrine and Krome soils have similar OC content but the TSNE model described atrazine sorption kinetics data well in Krome soil. Perrine is the only marl

Table 4. Effect of atrazine initial solution concentration on sorption kinetic parameters in Lauderhill soil, with standard error in parentheses.

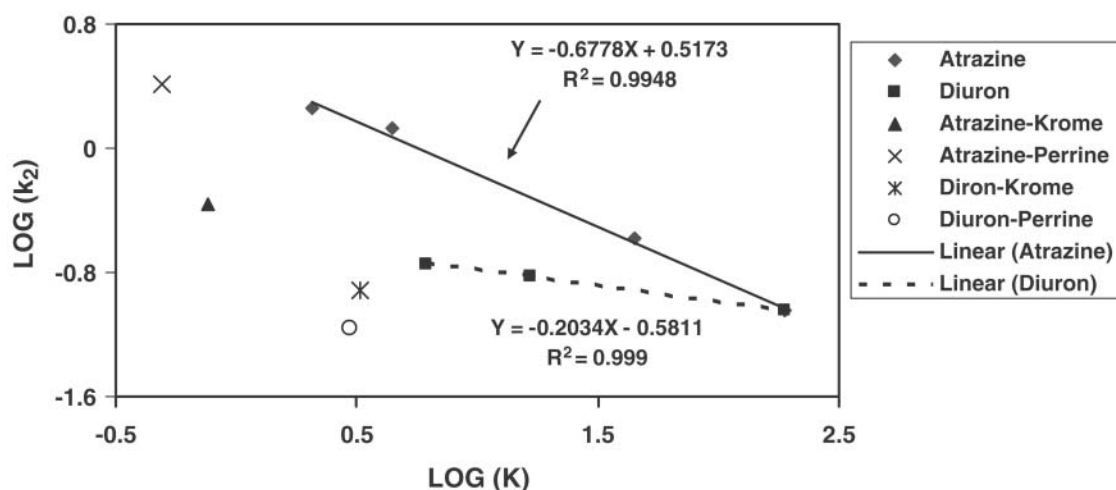| Concentration	k_2	K	F
µg mL^{-1}	h^{-1}	L kg^{-1}	
4	0.28 (0.05)	44.30 (2.02)	0.57 (0.05)
8	0.25 (0.06)	44.60 (1.21)	0.61 (0.05)
14	0.25 (0.03)	44.60 (0.69)	0.52 (0.08)
18	0.27 (0.03)	44.70 (1.16)	0.56 (0.02)
All concentrations	0.26 (0.03)	44.70 (0.90)	0.58 (0.03)

Fig. 6. Relationship between k_2 and K. The top line is for atrazine and the bottom line is for diuron. Two soils (Krome and Perrine) were excluded while calculating the correlation lines for atrazine and diuron.

soil among the carbonatic soils used in this study. The Lauderhill soil, which has the highest OC content, exhibited the slowest sorption kinetics (smallest k_2 values) for both pesticides. In Florida, Lauderhill soil is found in association with Chekika, Krome, and Perrine.

k_2–K Relationship

For soils that do not contain expanding clay minerals, sorption kinetics of neutral organic chemicals have been attributed to soil organic matter. Since organic matter is the predominant component of soils that adsorbs neutral organic chemicals, intra-organic matter diffusion has been proposed as the rate limiting mechanism for sorption kinetics (Khan, 1973; Brusseau et al., 1991). The fist-order desorption rate coefficient (k_2) is a lumped parameter which combines several processes that control mass transfer of sorbates into the organic matter matrix. These can include molecular size, molecular weight, hydrocarbonaceous surface area, total molecular surface area, diffusion path length, and makeup of organic matter that determines resistance to diffusion (Brusseau et al., 1991). The diffusion path length should increase with increase in organic matter content of the soil, which in turn should decrease the value of k_2. The sorption coefficient K should increase as the organic matter content of the soil increases.

The sorption parameters k_2 and K have been reported to be inversely related for sorption of neutral organic chemicals in soils and sediments (Karickhoff, 1980; Karickhoff and Morris, 1985; Rao et al., 1979; Brusseau et al., 1991). The data in Table 2 show that atrazine and diuron have many similar values of parameters that can affect the magnitude of k_2. However, the correlation lines between k_2 and K show that atrazine and diuron behaved differently in these five soils (Fig. 6). Atrazine and diuron seem to behave similarly in only the Lauderhill muck. For Webster and Chekika soils diuron and atrazine data were described by different correlations. In addition, for two carbonatic soils (Perrine and Krome) the k_2–K relationship for either atrazine or diuron does not describe the sorption kinetics data. In

Florida Chekika soils are transitional between well drained soils (Krome) and the poorly drained marl soils (Perrine). These data seem to imply that the makeup of organic matter in carbonatic soils is different from organic matter in noncarbonatic soils. This trend in sorption kinetics data can be used to further explain the low K_{oc} values that were calculated for atrazine and diuron in carbonatic soils.

Apparent Sorption Coefficient (K^*)

Data in Fig. 7 and 8 show examples of the apparent sorption coefficient (K^*) as a function of time for atrazine and diuron in Lauderhill and Chekika soils. The sorption coefficients asymptotically approached equilibrium K values in about 24 h. The TSNE model (Eq. [2]) describes the apparent sorption coefficient data reasonably well. Chen and Wagenet (1997) observed similar increase of atrazine adsorption in Niagara silt loam from 1 to 237 h. Their data indicated that adsorption did not reach equilibrium even after 237 h of incubation. In this
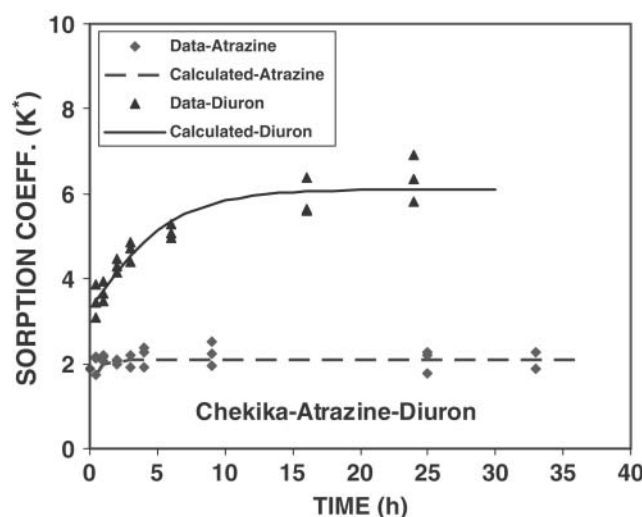

Fig. 7. Apparent sorption coefficient for atrazine and diuron in Chekika soil.
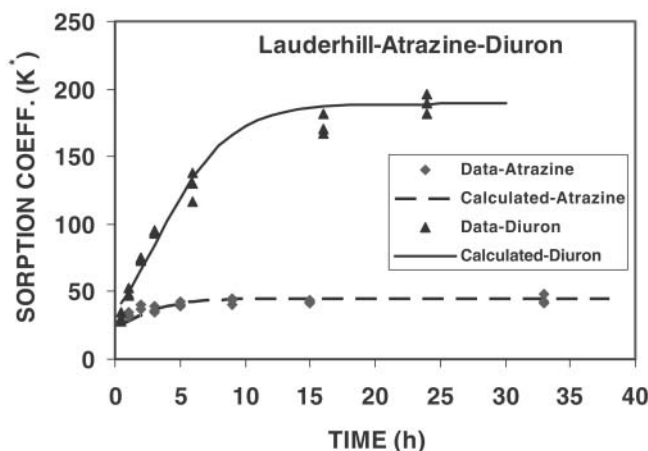
Fig. 8. Apparent sorption coefficient for atrazine and diuron in Lauderhill soil.

study, all soil–chemical combinations during the kinetics experiments reached equilibrium in 24 h or less. These data clearly show that sorption isotherms can be generated at any time, but the correct isotherm is the one that is measured at equilibrium. Sorption coefficient values calculated from isotherms that are not measured at equilibrium will underestimate sorption.

CONCLUSIONS

All three carbonatic soils (Krome, Chekika, and Perrine) adsorbed diuron and atrazine much less than the noncarbonatic soil (Webster) and the organic soil (Lauderhill) as evident from their K_{oc} values. This might be due to differences in the composition of organic matter in these soils. The TSNE sorption model described the sorption kinetics data well for all soil–chemical combinations except for Perrine–atrazine that seems to be described by the OSNE model. Perrine is the only soil characterized as a marl soil among the three carbonatic soils and contains the largest amount of $CaCO_3$. Diuron exhibited slower sorption kinetics (smaller k_2 values) than atrazine in all soils. The difference in sorption kinetics between atrazine and diuron increased with increase in soil OC content. The batch kinetics experiments were used to differentiate the behavior of two similar organic pesticides in five soils. The data were also used to point to the possible differences in organic matter makeup between carbonatic and noncarbonatic soils.

The K_{oc} values for atrazine and diuron obtained in this study for carbonatic soils were a third of the values reported literature for noncarbonatic soils. This implies that use of literature K_{oc} values for predicting fate and transport of similar pesticides in carbonatic soils would result in underestimation of pesticide travel times to ground water.

As a whole, the batch sorption kinetics experiments proved to be a useful tool in distinguishing the behavior of two organic pesticides in carbonatic and noncarbonatic soils and in identifying a potential difference in organic matter makeup between carbonatic and noncarbonatic soils. Further research is, therefore, war-

ranted to investigate the origin and nature of organic matter of these carbonatic soils.

APPENDIX

Figure 9 illustrates the two-site nonequilibrium (TSNE) batch sorption kinetics model. For the TSNE model linear sorption is assumed. All the solute is initially in solution.

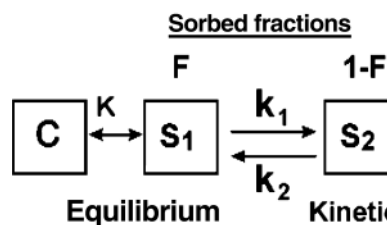**Fig. 9. The two-site nonequilibrium (TSNE) batch sorption kinetics model.**

Terms include:

Term	Definition	Unit
A	total mass of solute added to soil, always constant = VC_{in}	mg
C	solute concentration in the water	mg L^{-1}
C_{in}	initial, added solution concentration	mg L^{-1}
C^0	solution concentration after partitioning to the instantaneous site at $t = 0$	mg L^{-1}
C^∞	solution concentration at equilibrium	mg L^{-1}
S	total sorbed solute concentration = $S_1 + S_2$	mg kg^{-1}
S_1	sorbed solute concentration on the soil of the equilibrium region	mg kg^{-1}
S_1	$F\,KC$ at all times	mg kg^{-1}
S_2	sorbed solute concentration on the soil of the kinetic region	mg kg^{-1}
S_2^0	sorbed solute concentration on the soil of the kinetic region at ($t = 0$)	mg kg^{-1}
t	time	h
F	fraction of the total sorption in the Type 1 region when the system is in equilibrium	
K	linear sorption partition coefficient at equilibrium	L kg^{-1}
$K*$	apparent linear sorption partition coefficient before equilibrium	L kg^{-1}
V	volume of water	L
M	mass of soil	kg
k_1	kinetic rate coefficient for sorption to the Type 2 sites	1/h
k_2	kinetic rate coefficient for desorption from the Type 2 sites	1/h
R	retardation factor	
β	fraction of retardation for the instantaneous region	

Define:

$$R = 1 + \frac{M}{V}K \qquad C^0 = \frac{VC_{in}}{V + FMK} = \frac{C_{in}}{\beta R}$$

$$\beta = (1 + F\frac{M}{V}K)/R \quad C^\infty = \frac{VC_{in}}{V + MK} = \frac{C_{in}}{R}$$

The Solution for *C* versus Time

First at equilibrium (time = ∞) total sorption is given by:

$$S^\infty = S_1^\infty + S_2^\infty = KC^\infty \qquad [A1]$$

$$S_1^\infty = FKC^\infty \quad S_2^\infty = (1 - F)KC^\infty \qquad [A2]$$

Solute mass transfer from the Type 1 sites to the Type 2 sites is given by:

$$\frac{\partial S_2}{\partial t} = k_1 S_1 - k_2 S_2 \qquad [A3]$$

which implies at time $= \infty$:

$$k_1 = k_2 \frac{(1 - F)}{F} \qquad [A4]$$

The total solute mass, A (mg), added to the soil is constant and is given by:

$$A = VC + MS_1 + MS_2 = (V + MFK)C + MS_2 \quad [A5]$$

$$A = (V + MFK)C^0 + MS_2^0 \text{ at time} = 0 \qquad [A6]$$

At any given time, S_2 is given in terms of C by:

$$MS_2 = A - (V + MFK)C \qquad [A7]$$

And at equilibrium, time $= \infty$, where $S_2 = (1 - F)KC$, the equilibrium solution concentration is given by:

$$C^\infty = \frac{A}{(V + MK)} \qquad [A8]$$

The basic equations for this system are:

$$(V + MFK)\frac{dC}{dt} = k_2 MS_2 - k_1 MS_1 \qquad [A9]$$
$$= k_2 MS_2 - k_1 MFKC$$

$$M\frac{dS_2}{dt} = k_1 MS_1 - k_2 MS_2 \qquad [A10]$$

By substituting for k_1 from Eq. [A4] and for S_2 from Eq. [A7], Eq. [A9] becomes:

$$(V + MFK)\frac{dC}{dt} = k_2[A - (V + MK)C] \qquad [A11]$$

The solution to Eq. [A11] in terms of C is:

$$(V + MK)C - A = [(V + MK)C^0 - A] \exp\left[-\left(\frac{k_2}{\beta}\right)t\right]$$
$$[A12]$$

where β is given by:

$$\beta = \frac{V + MFK}{V + MK} \qquad [A13]$$

By using Eq. [A8] for C^∞, Eq. [A12] can be rearranged to:

$$C = C^\infty + (C^0 - C^\infty) \exp\left[-\left(\frac{k_2}{\beta}\right)t\right] \qquad [A14]$$

Sorption Experiment

Water with solute at concentration C_{in} is added to soil containing no sorbed solute. Thus solute mass, $A = VC_{in}$. The solute partitions instantly to sites of Type 1 such that:

$$C^0 = \frac{VC_{in}}{V + MFK} = \frac{C_{in}}{\beta R} \qquad [A15]$$

$$S_1 = FC^0 \qquad [A16]$$

$$S_2 = 0 \qquad [A17]$$

$$C^\infty = \frac{VC_{in}}{V + MK} = \frac{C_{in}}{R} \qquad [A18]$$

With these substitutions into Eq. [A14] the solution becomes:

$$\frac{C}{C_{in}} = \frac{1}{R} + \left(\frac{1}{\beta R} - \frac{1}{R}\right) \exp\left[-\left(\frac{k_2}{\beta}\right)t\right] \qquad [A19]$$

The three parameters (F, k_2, and K) are determined from the data using nonlinear curve fitting procedures on the C/C_{in} vs. time data. Thus a series of experiments with different C_{in} is normalized to one line by plotting C/C_{in} vs. time.

Apparent Sorption Coefficient (K^*)

The term S vs. time is given by:

$$S = \frac{V}{M}(C_{in} - C) \qquad [A20]$$

$$K^* = \frac{S}{C} = \frac{V}{M}\left(\frac{C_{in}}{C} - 1\right) \qquad [A21]$$

Using C/C_{in} obtained in Eq. [A19], the apparent sorption coefficient (K^*) in Eq. [A21] can be calculated as a function of time in Eq. [A22]:

$$K^* = \frac{V}{M}\left\{\left[\frac{1}{R} - \left(\frac{1}{R} - \frac{1}{\beta R}\right) \exp\left(-\frac{k_2 t}{\beta}\right)\right]^{-1} - 1\right\} \quad [A22]$$

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